Short communication

Sinusoidal potential cycling operation of a direct ethanol fuel cell to improving carbon dioxide yields

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HIGHLIGHTS

- Sinusoidal potential cycling increases selectivity for the oxidation of ethanol to CO_2.
- This can increase the efficiency of direct ethanol fuel cells.
- The benefits of potential cycling will be higher for catalysts with better selectivity for C–C bond breaking.
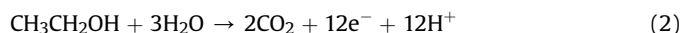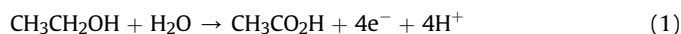
ARTICLE INFO

ABSTRACT

A direct ethanol fuel cell has been operated under sinusoidal (AC) potential cycling conditions in order to increase the yield of carbon dioxide and thereby increase cell efficiency relative to operation at a fixed potential. At 80 °C, faradaic yields of CO_2 as high as 25% have been achieved with a PtRu anode catalyst, while the maximum CO_2 production at constant potential was 13%. The increased yields under cycling conditions have been attributed to periodic oxidative stripping of adsorbed CO. These results will be important in the optimization of operating conditions for direct ethanol fuel cells, where the benefits of potential cycling are projected to increase as catalysts that produce CO_2 more efficiently are implemented.

1. Introduction

Direct ethanol fuel cells (DEFCs) based on proton exchange membrane (PEM) technology are attractive as part of a long-term renewable energy strategy because of their high theoretical efficiency (97% [1]) together with the ready availability and high energy density of bioethanol [2,3]. However, their high anode overpotentials, crossover of ethanol to the cathode, and incomplete oxidation of ethanol to acetaldehyde and acetic acid currently make them impractical.

The most serious of these issues is the formation of acetic acid, which cannot be oxidized further under PEM DEFC operating conditions [4]. This decreases the energy efficiency greatly because only 4 electrons are passed per ethanol molecule (Eq. (1)) relative to 12 for the complete oxidation to CO_2 (Eq. (2)).

$$CH_3CH_2OH + H_2O \rightarrow CH_3CO_2H + 4e^- + 4H^+ \tag{1}$$

$$CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 12e^- + 12H^+ \tag{2}$$

The efficiency for the complete oxidation can be monitored and assessed by measuring the faradaic yield of CO_2 produced by the cell, given by Eq. (3),

$$CO_2 \text{ yield} = 6 \text{ F mol}_{CO_2}/Q \tag{3}$$

where mol_{CO_2} is the moles of CO_2 produced and Q is the charge passed. The yield of CO_2 has been found to depend strongly on the catalyst employed, temperature, ethanol concentration, and current (or cell potential) [2,4,5]. The yield of CO_2 increases with increasing temperature, decreases as the ethanol concentration is increased, and generally has been found to decrease with increasing current (decreasing cell potential) [5]. It has been reported that pulsing of the current applied to an ethanol electrolysis cell can increase the CO_2 yield by promoting the oxidation of adsorbed intermediates at a high current while ethanol adsorbs

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and dissociates at open circuit [6]. Pulsing has also been applied to hydrogen [7] and methanol fuel cells [8] to mitigate CO poisoning. That principle has been applied here to the operation of a PEM DEFC by using a sinusoidal (AC) potential waveform.

2. Experimental

Anhydrous ethanol (Commercial Alcohols Inc.) was used as received and double distilled water was used throughout all experiments. Cathodes consisted of 4 mg cm^{-2} Pt black on Toray™ carbon fiber paper; anodes consisted of 5.5 mg cm^{-2} PtRu black on Toray™ carbon fiber paper. Nafion™ 117 membranes (Dupont) were cleaned at 80 °C in 3% H_2O_2(aq) and 1 M H_2SO_4(aq), rinsed with water, and stored in water.

A 5 cm^2 commercial fuel cell (Fuel Cell Technology Inc.) was used. Membrane and electrode assemblies were prepared by pressing (room temperature; ca. 1.5 MPa) a 5 cm^2 anode and a 5 cm^2 cathode onto a Nafion™ 117 membrane in the cell [9]. The cell was operated with an anode feed of 0.10 mol L^{-1} ethanol solution at 0.69 mL min^{-1}. The cathode feed was air at 20 mL min^{-1}. The cell was operated with a Hokuto Denko HA-301 potentiostat with the sinusoidal voltage generated by a Solartron 1250 frequency response analyzer. For CO_2 analysis both the anode solution and the cathode gas were passed into a 125 mL flask to collect the liquid. The gas stream exiting the flask was passed through a Telaire 7001 non-dispersive infrared CO_2 detector [10]. The CO_2 traces have been corrected for the delay in the detector response due to tubing and flask, and the background reading prior to passing current though the cell, due to CO_2 produced by the chemical reaction of ethanol and O_2 arising from crossover of both through the membrane [11,12].

3. Results and discussion

Fig. 1 shows how the cell voltage was varied, and the corresponding current as a function of time, in an experiment at a bias potential of 0.4 V, frequency of 0.1 Hz, and amplitude (rms) of 0.1 V. An expanded section towards the end of the experiment is shown, to illustrate the steady-state behavior. The average current over this

period was 73 mA, while an average of 79 mA was obtained over the full 1200 s of the experiment.

It can be seen from Fig. 1 that the current dropped to close to zero at the cell potential peaks. During this part of the cycle, ethanol will adsorb and dissociate on the electrode with limited production of undesirable products (acetaldehyde and acetic acid) because the current is low. At the minima in the cell potential, the current was high with a significant contribution due the oxidation of adsorbed CO, as demonstrated by *in situ* infrared spectroscopy [13] and mass spectrometry [14]. This leads to enhanced selectivity for the complete oxidation of ethanol to CO_2 as illustrated in Fig. 2, which compares CO_2 *vs.* time traces for operation of the cell as in Fig. 1 and for operation at a constant potential of 0.4 V. Here, the much higher concentration of CO_2 exiting the cell during AC potential cycling indicates that more ethanol was oxidized completely to CO_2. Although the average current was slightly lower in the constant potential experiment (60 mA *vs.* 79 mA), it is very clear from the data in Fig. 2 that the CO_2 yield was significantly higher in the AC experiment. Based on the charge passed and the moles of CO_2 produced (moles $CO_2 = \int(\text{ppm}_{CO_2} \cdot \dot{\eta}/10^6)dt$, where $\dot{\eta}$ is the N_2 flow rate in mol s^{-1}) over the full runs, the average CO_2 yields calculated using Eq. (3) were 17.8% for AC operation and 9.8% at constant potential. However, these values are underestimated because of the long time (ca. 600–800 s) required for the CO_2 level in the collection flask to approach equilibrium. More accurate steady-state yields of 25.6% for AC operation and 11.6% at constant potential were therefore estimated (Eq. (3)) by integrating the current (Fig. 1) and CO_2 readings (Fig. 2) over just the final 200 s (i.e. 900–1100 s). The much higher steady-state CO_2 yield obtained under AC operation indicates that a higher fraction of the ethanol consumed underwent the complete 12 electron oxidation to CO_2. Consequently, it can be inferred that a lower fraction was oxidized to the acetaldehyde and acetic acid byproducts. Although these results do not provide any direct mechanistic information, it can be inferred from previous mechanistic studies [13,14] that oxidation of adsorbed CO contributed significantly to the enhanced CO_2 yield. During each potential cycle, this CO would have been replenished at high cell potentials by partial oxidation of ethanol flowing through the cell [6].
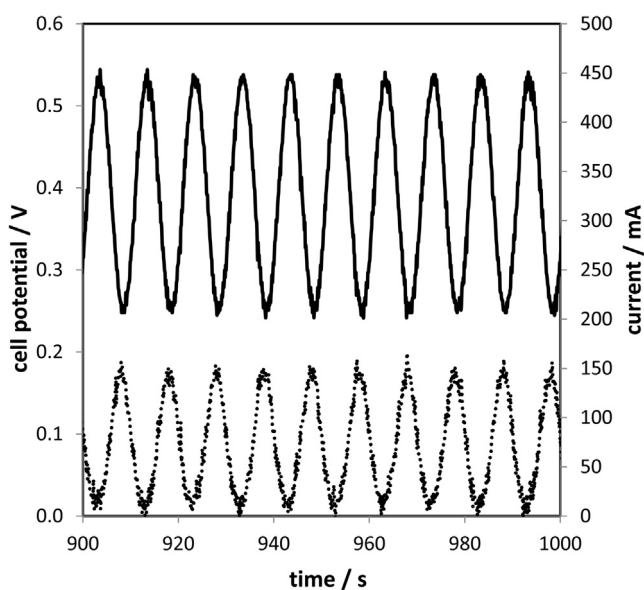

Fig. 1. Cell potential (solid) and current (dotted) *vs.* time plots for operation of a DEFC at 80 °C under AC potential cycling conditions. Potential bias = 0.4 V; frequency = 0.1 Hz; amplitude = 0.1 V rms.
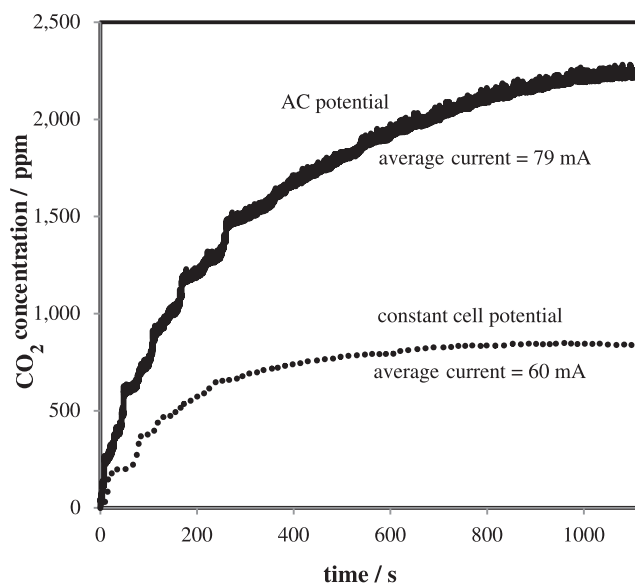

Fig. 2. CO_2 concentration *vs.* time plots for the combined anode and cathode exhaust streams from a DEFC at 80 °C at a constant potential of 0.4 V (dotted) and under AC potential cycling conditions (solid; bias = 0.4 V; frequency = 0.1 Hz; amplitude = 0.1 V rms).

The mechanism of the electrochemical oxidation of ethanol at Pt based electrodes is still under intensive experimental [15,16] and theoretical [17] investigation [5]. The main initial pathway involves partial oxidation of adsorbed ethanol to adsorbed acetaldehyde, which can desorb as the first product [18]. However, further oxidation (dehydrogenation) can easily occur to an adsorbed acetyl species (CH_3CO_{ads}), which is the common intermediate for both acetic acid and CO_2 formation [17,18]. One of these theoretical studies [17] "highlights the need for careful control of oxidant surface coverage that will allow facile C–C bond cleavage while still providing sufficient levels of CO oxidation". The results shown in Fig. 2 demonstrate that this can be achieved to a significant extent by potential cycling.

A series of additional experiments were performed in order to explore whether higher yields could be obtained under other AC operation conditions, and to check whether the difference in the average current contributed to the difference in CO_2 yields between the two sets of data in Fig. 2. Bias potential from 0.3 to 0.4 V were used because this is the optimum operating potential range. At higher potentials the current is too low to be very useful, while lower potentials are not very useful and produce much lower cell efficiencies. The results are summarized in Table 1. It can be seen from these results that decreasing the DC potential increased the average current, but did not have a significant effect on the CO_2 yield. AC operation of the cell at a lower bias potential and lower frequency resulted in lower CO_2 yields, although they were still significantly higher than any obtained at constant potential. Changing the amplitude at 0.35 V did not change the average current nor CO_2 yield significantly. These experiments, and a number of others that are not reported here, indicated that the cycling conditions in Fig. 1 were close to optimum for the cell and other operating conditions employed in this work.

Fig. 3 compares a polarization curve for the cell with current and voltage data from Fig. 1. The current during AC operation doesn't track the steady-state current exactly because of the charging current due to the double layer capacitance of the electrodes. The average current at most potentials is slightly higher under AC operation indicating improved cell performance under cycling conditions. This is most notable at high currents, while the cell underperforms at low currents during AC cycling.

The highest percentage increase in CO_2 yield obtained in this work was 121%, for the experiments at 0.4 V shown in Figs. 1 and 2. Although this appears to be substantial, its effect on the efficiency of the cell is much lower because of the nature of the relationship between CO_2 yield and efficiency, and also because AC operation of the cell decreases the potential efficiency. If we neglect the effects of crossover, the overall efficiency (ε_{cell}) of a DEFC is given by Eq. (4) [13],

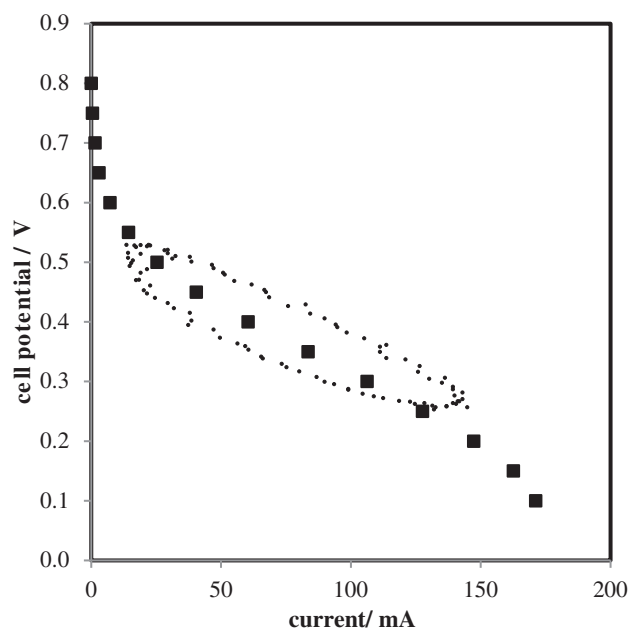$$\varepsilon_{cell} = \varepsilon_{rev} \times \varepsilon_E \times \varepsilon_F \tag{4}$$

Fig. 3. Polarization curve (■; current averaged over 1 min after 4 min at each potential) and current *vs.* potential for AC potential cycling (dotted; potential bias = 0.4 V; frequency = 0.1 Hz; amplitude = 0.1 V rms).

where ε_{rev} is the theoretical efficiency (97%), ε_E is the potential efficiency (E_{cell}/E_{rev} where E_{rev} is the reversible cell potential of 1.44 V under the conditions used here), and ε_F is the faradaic efficiency given by Eq. (5),

$$\varepsilon_F = (2 \times \%_{CH_3CHO} + 4 \times \%_{CH_3CO_2H} + 6 \times \%_{CO_2})/(\%_{CH_3CHO} + \%_{CH_3CO_2H} + \%_{CO_2}/2)/12 \tag{5}$$

where the % terms are the faradaic yields of each of the three major products.

Faradaic efficiencies calculated using Eq. (5) are plotted in Fig. 4 as a function of the CO_2 yield for various ratios of acetaldehyde to
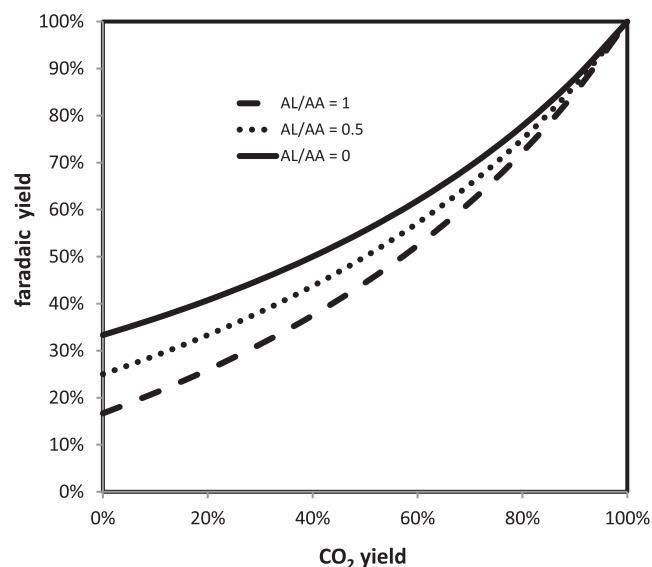

Fig. 4. Theoretical relationships between faradaic efficiency and CO_2 yield at acetaldehyde (AL): acetic acid (AA) ratios of 1.0 (solid), 0.5 (dotted), and 0 (dashed).

Table 1
Summary of data for operation of a DEFC at 80 °C at constant potential and under AC potential cycling conditions. Currents and yields are averages after 900 s of operation.

DC potential/V	Frequency/Hz	Amplitude/V	Average current/mA	Average CO_2 yield
0.30	No AC		106	13.0%
0.30	0.05	0.12	131	14.5%
0.35	0.03	0.12	93.1	16.4%
0.35	0.03	0.13	89.8	17.9%
0.35	0.03	0.15	103	16.8%
0.40	No AC		57.5	11.6%
0.40	0.1	0.1	72.0	25.6%

acetic acid. It can be seen that increasing the yield of CO_2 has a much greater effect on the cell efficiency at high CO_2 yields. For the data in Table 1 at 0.4 V, and assuming an acetaldehyde:acetic acid ratio of 0.67 [11], ε_F was 27% at constant potential and increased to 34% under AC cycling. However, the potential efficiency (weighted for the moles of ethanol converted at each potential during cycling) decreased from 35% to 29% when the potential was cycled because more ethanol was oxidized at lower cell potentials. Overall, cycling increased the cell efficiency (Eq. (4)) from 9.2% to 9.6%. Although not large, this 5% increase in cell efficiency was achieved with a 25% increase in the average current (Table 1) and a 4.3% increase in average power.

From a practical point of view, the PtRu catalyst used here is not suitable for use in DEFCs because of the low yields of CO_2 that it produces. Pure Pt produces much higher CO_2 yields than PtRu because it promotes C–C bond cleavage, but its potential efficiency is lower because higher potentials are needed to oxidize CO [5,19]. Other alloy catalysts such as PtSn can deliver higher potential efficiency as well as improved CO_2 yields [5]. Fig. 4 shows that the benefits of AC cycling would be higher for such catalysts because of the higher slopes at higher CO_2 yields. Increasing the cell temperature would also increase CO_2 yields [2] and this should also increase the benefits of AC cycling.

4. Conclusions

It has been demonstrated that potential cycling with a sinusoidal waveform can greatly increase the yield of CO_2 produced by a DEFC, and that this leads to a significant increase in the faradaic efficiency of the cell. Although this is partially offset by a decrease in potential efficiency, there can be a net benefit in overall cell efficiency, and/or power density. It is demonstrated, in theory, that AC cycling (or other potential modulation) of DEFCs with better catalysts has the potential to significantly enhance their efficiencies. This could be a significant factor in their commercialization.

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